STUDIES IN SPECTROPHOTOMETRIC ANALYSIS

BY

GORDON OWEN GUERRANT

A.B., Westminster College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

The urgent need of an extremely rapid, sensitive and selective method for the determination of certain elements, particularly the alkali and alkaline earths, has led to interest in spectrophotometric analysis by flame procedures and the development of the flame spectrophotometer (1,2,3). The procedures are finding increased acceptance and are slowly displacing the more troublesome methods for the analysis of soils, water and oils, and plant, biological, inorganic and organic materials. The present investigation has been concerned with the use of one of the newer instruments, the Beckman Flame Spectrophotometer for quantitative analysis.

The instrument measures photoelectrically the emission of an element at a particular wavelength when a solution of the element is atomized into a mist under carefully controlled conditions and excited in the flame of an oxygen-gas burner. The existing procedures of quantitative analysis (1,4) did not yield results of highest accuracy with this equipment. Additional information (5) was desired as to interferences by the presence of foreign ions, particularly when the propane-oxygen flame was used for excitation.

Experimental And Results

A lack of consistency of performance of the equipment made necessary a detailed study of factors responsible for the trouble and required the development of techniques to minimize the difficulties. The following factors have been studied: pressure regulation of gas, oxygen and air; instrument stability; spray chamber condition; contamination of samples; care of atomizer capillary; differences in atomizers; flame background characteristics; slit width adjustment; wavelength selection; influence of various solvents. Directions are given for reducing errors from these sources.

Careful regulation of pressures is required to obtain consistent results. Instrument stability is increased by installation of a container of magnesium perchlorate to absorb moisture from the photo-tube compartment. Salt formation upon the walls of the spray chamber is found to markedly decrease the intensity of the element. Samples are contaminated by liquid adhearing to the outside of the atomizer capillary if it is dipped too deeply into the sample solution. A change of atomizers is found to give different intensity values and also different ratios by the internal standard procedure. The flame gives a high background at 309 $m\mu$ and 975 $m\mu$ which makes investigations in these regions difficult. The wavelength value changes with temperature. This requires frequent calibration and very careful setting when narrow slit widths are employed.

The absolute procedure of analysis has been examined. It is based upon the use of a working curve correlating the intensity value of a selected line of the element sought with the respective known concentrations of the element. This procedure did not yield results of desired accuracy because it is subject to error from fluctuations in gas, oxygen and air pressures, and changes in the photoelectric response of the instrument, partial clogging of the atomizer capillary and interferences from the presence of foreign ions. Two modified flame procedures have been developed and evaluated.

The internal standard procedure consists of the addition of a definite amount of some element which is excited in the same manner as the unknown. By a comparison of the intensities produced by the unknown and standard, a compensation is made for the variables that exist. With the Beckman equipment this procedure required frequent changes in instrument wavelength settings to alternately record the unknown and standard intensity several times. To make the adjustment quickly one must operate with a slit of such width that the intensity maximum falls well within the nominal spectral band width. An auxiliary diaphragm was designed and installed in the optical path of the instrument to reduce the

initial intensity of light entering the instrument and permit the use of wider slit widths. Some internal standards were considered for potassium. Sodium was eliminated because of its probable occurrence in unknown samples of potassium, and rubidium was eliminated because its principal emission line interferes with that of potassium at wide slit widths. A comparison of lithium and cesium showed that the latter gave the best results.

The standard addition procedure was developed for use where no suitable internal standard had been found. It consists in relating the intensity of the selected emission line of the element to the intensity increase produced when a known amount of the same element is added to the unknown. This standard addition of element was influenced to the same degree by foreign ions present in the solution, thus a compensation was made for their presence. Any differences in instrument operating conditions were eliminated by making several consecutive readings upon the unknown and the unknown plus the standard addition.

The reliability of the three procedures of analysis for the determination of potassium with no interfering ions present has been evaluated. The standard deviation was found to be $\pm$ 3.9% for the absolute procedure, $\pm$ 2.1% for the internal standard procedure and $\pm$ 2.8% for the standard addition procedure.

The influence of extraneous acids upon the determination of potassium has been studied. Hydrochloric, nitric, oxalic and boric acids have only a slight effect upon the results obtained for potassium by the absolute procedure and much less by the internal standard procedure. Sulfuric, perchloric and phosphoric acids have a pronounced effect upon the results obtained. The effect of phosphoric acid has been found to decrease the flame intensities of the alkali metals. The greatest effect was noted upon cesium and the least effect upon lithium. The intensity of the flame spectrum of an alkali metal was increased by the presence of another alkali.

The determination of boron, manganese, cobalt and copper in trace amounts were shown to be practical by flame spectrophotometry. The use of small volumes of low concentration makes this procedure desirable, since many samples may be concentrated to small volumes in order to obtain increased sensitivity for elemental detection. The limit of minimum detectability appears to be as follows: boron, one part per million; manganese, one-fifth part per million; cobalt, one-half part per million; copper, one part per million. The determination of copper in municipal water supplies by flame spectrophotometry has unusual promise in regard to speed and convenience.

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VITA

The author was born July 11, 1923, at Fulton, Missouri, and received his primary and secondary education there. After graduating from high school in 1941, he entered Westminster College. He served as laboratory assistant in chemistry, attending there until June, 1944, when he received the degree of Bachelor of Arts.

The author entered military service as an Ensign in the U. S. Naval Reserve in September, 1944, and was released to inactive duty in June, 1946.

In December, 1944, he was married to Jane Bush.

In June, 1946, he entered the Graduate College of the University of Illinois and served as a teaching assistant in the Division of Analytical Chemistry.

The author is a member of the American Chemical Society, Sigma Xi, and Alpha Chi Sigma.

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